PART ONE

SUBSTITUTED QUINONEDIIMINES

PART TWO

RESTRICTED ROTATION IN CERTAIN AROMATIC AMINES

BY

ANANT SHANTARAM NAGARKATTI

B.Sc., University of Bombay, 1942
B.Sc. (Tech)., University of Bombay, 1945
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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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PART ONE

SUBSTITUTED QUINONEDIIMINES

Introduction

The first satisfactory preparation of *p*-quinone mono- and di-imines was reported by Willstätter (1) and later by Kehrmann and Cordone (2). They obtained these compounds by the oxidation of *p*-aminophenol and *p*-phenylenediamine with dry silver oxide in dry ether. These, however, were unstable to light and acids and polymerized with ease. Many N-alkyl, N, N′-dialkyl and ring substituted *p*-quinone mono- and di-imines are also known and these have been reported to be slightly more stable than the unsubstituted ones. The reactions of such compounds have remained unexplored because of the difficulty of their preparation and their instability.

The present investigation was undertaken when the N, N′-dibenzenesulfonyl derivative of *p*-quinonediimine was found to be comparatively more stable than the compounds prepared before. The purpose of this investigation was to study the scope and limitations of various oxidizing agents as preparative reagents for substituted quinonediimines. It was also found to be of interest to study the reactions of these substituted quinonediimines especially with a view to compare them with those of *p*-benzoquinone.

Discussion of Results

N, N′-Dibenzenesulfonyl-*p*-phenylenediamide was oxidized to the corresponding *p*-quinonediimide by the action of silver oxide. In ether the reaction was slow and unsatisfactory. In acetone, however, a 50 per cent yield of the product was obtained. Bromine in pyridine was found to be an efficient oxidizing agent only for N, N′-dibenzenesulfonyl- 2, 5-dimethyl-*p*-phenylenediamide. Chromic acid or sodium dichromate in glacial acetic acid yielded better results. The best and the most effective procedure of all was found in the use of lead tetraacetate in acetic acid at room temperature or at somewhat higher temperatures. Using this oxidizing agent the following derivatives of *p*-quinonediimines and of monoimine were obtained from the corresponding derivatives of *p*-diamines and *p*-aminophenol:—

N, N′-Dibenzenesulfonyl derivatives of 2-chloro- and 2, 5-dimethyl-3-chloro-*p*-quinonediimine, N, N′-di-*p*-toluenesulfonyl-*p*-quinonediimide, N, N′-dimethanesulfonyl-*p*-quinonediimide and N-benzenesulfonyl-*p*-quinonemonoimide.

The action of various reagents on N, N′-dibenzenesulfonyl-*p*-quinonediimide was studied. It was quantitatively reduced to N, N′-dibenzenesulfonyl-*p*-phenylenediamide by hydrogen in presence of platinum, zinc and acetic acid, and hydriodic acid. Sulfur dioxide and sodium hydrosulfite in water also reduced the compound in good yields.

Hydrogen chloride added presumably 1, 4 followed by rearrangement, since N, N′-dibenzenesulfonyl-2-chloro-*p*-phenylenediamide was obtained in quantitative yields. In a similar manner the N, N′-dibenzenesulfonyl derivatives of 2, 5-dimethyl-3-chloro- and 2, 5-dimethyl-3, 6-dichloro-*p*-phenylenediamine were obtained from the corresponding derivatives of 2, 5-dimethyl- and 2, 5-dimethyl-3-chloro-*p*-quinonediimine. Attempts to reduce the substituted quinonediimine with stannous chloride or zinc chloride in concentrated hydrochloric acid yielded predominantly N, N′-dibenzenesulfonyl-2-chloro-*p*-phenylenediamide. The same product was obtained even by boiling with 10 per cent hydrochloric acid. Hydrogen bromide, on the other hand, was oxidized to bromine.

The most surprising reaction was the one in which the *p*-quinonediimide was reduced to N, N′-dibenzenesulfonyl-*p*-phenylenediamide by hot dilute sulfuric acid or cold dilute alkali.

Chlorine added to the substituted quinonediimine in chloroform solution but the addition product could not be readily purified. The analysis indicated a trichloro derivative which might have been caused by the addition of four atoms of chlorine and the subsequent elimination of a molecule of hydrogen chloride. Bromine similarly gave a crystalline product but did not give a perfect analysis for a dibromo derivative.

All the substituted quinonediimines gave characteristic color reactions with concentrated sulfuric acid.

Conclusion

The reactions of N, N′-dibenzenesulfonyl derivatives of *p*-quinonediimines are comparable to those of *p*-benzoquinone except in the case of hydrogen bromide, dilute sulfuric acid, aqueous alkali and the comparative ease of addition of hydrogen chloride.

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PART TWO

RESTRICTED ROTATION IN CERTAIN AROMATIC AMINES

Introduction

Mills and Kelham (1) reported the successful resolution of N-acetyl-N-methyl-8-aminonaphthalene-1-sulfonic acid. They also noted that the brucine salt of N-acetyl-N-methylorthanilic acid mutarotated in chloroform. The object of the present work was to investigate whether a methyl or a carboxymethyl and a benzenesulfonyl groups on the nitrogen with a methyl ortho to it, could cause restriction of rotation.

Discussion of Results

N-Benzenesulfonyl-N-carboxymethyl-*o*-touidide was prepared by refluxing an ethanolic alkaline solution of N-benzenesulfonyl-o-toluidide with methyl bromoacetate, and the hydrolysis of the resulting product. The cinchonidine salt of this acid was obtained in crystalline form, but it failed to yield any isomers. Since mutarotation was observed only once, it was considered likely that the salt racemized even under mild conditions.

N, N′-Dibenzenesulfonyl-N, N′-dimethyl derivatives of 2, 4- and 4, 6-diamino-*m*-xylenes and of 2,5-diamino-*p*-xylene were prepared. These failed to yield *cis* and *trans* isomers. The separation of 2, 4- and 4, 6-diamino-*m*-xylenes in pure state from their mixture is described in the Appendix. For the preparation of 2, 5-diamino-*p*-xylene a modification of the processes of Schaumann (2), Noelting and coworkers (3) and Fisher and Walling (4), was employed.

The effect of introducing halogen in 3 and 6 positions of N, N′-dibenzenesulfonyl-2, 5-dimethyl-*p*-phenylenediamide was also studied. N, N′-Dibenzenesulfonyl-2, 5-dimethyl-3, 6-dichloro-*p*-phenylenediamide was methylated with methyl iodide in alkaline medium. The *cis* and *trans* isomers of the resulting compound were isolated.

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APPENDIX

2, 4- and 4, 6-Dinitro-*m*-xylenes have always been obtained as a mixture, by the nitration of *m*-xylene (1). When crystallized from ethanol the product gives a crystalline material usually melting at 57-62° which is not changed by further crystallization. Morgan (1) separated the mixed diamines resulting from the reduction of the mixture of dinitro-*m*-xylenes, by a tedious and time-consuming procedure.

In the present work the pure 2, 4-dinitro-*m*-xylene (m.p. 84°) was isolated from the mixture by three crystallizations from chloroform. The mixture of the dintro isomers was quantitatively reduced to the diamines, by hydrogen in presence of Raney nickel. The dihydrochloride salts were prepared and fractionally crystallized from water. The less soluble fractions were made alkaline, the bases extracted with ether and the ether evaporated. The fractionation was followed by determining the melting points of these bases at each stage. The less soluble fractions yielded 2, 4-diamino-*m*-xylene (m.p. 65-66°). The more soluble fractions when similarly treated gave 4, 6-diamino-*m*-xylene (m.p. 104°). The separation was almost quantitative.

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VITA

The author was born in Karwar, Bombay, India, on December 2, 1921. He graduated from the Government High School, Karwar, in 1938. The same year he entered the University of Bombay, and received the degree of Bachelor of Science in Chemistry in 1942. During 1942-1943 he was engaged in investigations on anacardic acid, in the Department of Chemical Technology of the University of Bombay. In 1943 he started studies as a graduate student in the same department and was awarded the degree of Bachelor of Science in the Technology of Intermediates and Dyes in 1945. Thereafter he was employed as a Fellow of the Board of Scientific and Industrial Research (India) for research on halogenated vat dyes. He was awarded a scholarship by the Government of Bombay for study in the U. S. A. in 1946. He entered the Graduate College of the University of Illinois in March, 1947, and received the degree of Master of Science in June, 1948.